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Accelerator mass spectrometry: state of the art and perspectives

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ABSTRACT

Accelerator mass spectrometry (AMS) is sometimes called ‘the art of counting atoms one by one’. In addition to counting individual atoms, AMS is also capable to determine both mass number (A) and atomic number (Z). Since an atom (also called a nuclide) is unambiguously characterized by the proton number (Z) and the neutron number ($N = A - Z$), a rare nuclide can be well separated from possible background events, and extremely low abundances of specific nuclides can be measured. In general, the use of an accelerator system as a mass spectrometer improves the isotope abundance sensitivity by many orders of magnitude as compared to standard mass spectrometry (without an accelerator). In particular, AMS provides the means to measure minute traces of long-lived radioisotopes of cosmogenic and/or anthropogenic origin in essentially every domain of our environment at large. This allows one to use AMS for performing research in many different areas, ranging from archaeology to astrophysics. In this review, an update of the current status of AMS and an outlook to future developments in both technical and applied aspects will be presented.

ARTICLE HISTORY

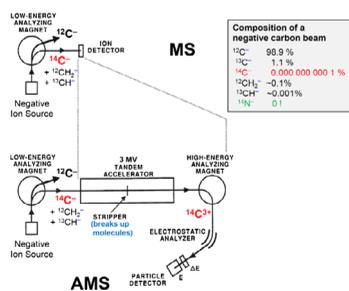
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The transition from Mass Spectrometry (MS) to Accelerator Mass Spectrometry (AMS)

1. Introduction

Today, it is an almost trivial statement to say that matter consists of atoms. And if we are capable of decomposing a piece of matter into its atoms and identifying and counting them one by one, we know its composition at the most basic level. However, this is rarely done starting from a raw piece of matter, because in general the elemental and isotopic composition is too complex to be sorted out in one step. Rather, the first step involves a variety of physical and chemical procedures to extract a particular element of interest from the original material, either in its pure form or as some chemically stable compound. This is the starting material for mass spectrometry (MS), which then determines the isotopic composition of the element of interest. MS is an analytic method known since more than hundred years [1], when ^{22}Ne was discovered as an additional isotope of ^{20}Ne . In 2013, the centennial anniversary of MS was celebrated by a special volume of the International Journal of Mass Spectrometry [2]. Over the past hundred years, MS (without an accelerator) became an enormously successful technique to measure stable isotope abundances reaching precisions at the ppm level in recent years (e.g. [3]). However, both inorganic MS and the rapidly expanding field of molecular MS are mainly restricted to atoms or molecules built by stable isotopes. The extremely low isotopic abundances of cosmogenic isotopes such as ^{14}C ($^{14}\text{C}/^{12}\text{C} \leq 1 \times 10^{-12}$) were beyond the capability of MS [4]. This changed in the late 1970s, when accelerators became an integral part of mass spectrometers [5–8]. A schematic presentation of the transition from MS to accelerator mass spectrometry (AMS) is shown in Figure 1.

AMS is a spin-off from nuclear physics research with accelerators, and a technique which allows one to measure extraordinary low isotopic ratios in the range from 10^{-12} to 10^{-16} by counting and identifying atoms in an accelerated ion beam. The large dynamic range is possible, because the abundant component, usually a stable isotope, is measured through an ion current (e.g. $16 \mu\text{A} = 1 \times 10^{14}$ ions/s) in suitable Faraday cups, whereas the rare isotopic component, often a long-lived radioisotope, is measured by single-atom counting (e.g. 10^2 – 10^{-2} ions/s) in detector systems common for nuclear physics experiments (e.g. gas ionization chambers). In some cases counting may be as low as 10^{-4} ions/s. Since in most cases both the mass and the nuclear charge of the rare ions can be determined, a unique characterization (A and Z) of the counted ion is possible. This is important if one aims at measuring extremely low isotopic abundances, where interference from unidentified ions is the limiting background in standard MS.

AMS has been reviewed many times since its invention in the late 1970s. The most recent reviews give a good overview of technical developments [9] and applications [10] of AMS. In addition, the proceedings of the tri-annual AMS conferences summarize recent developments in the field around the world. The last conference of this series took place in 2014 at Aix-en-Provence [11]. Because of the rich literature already available of both technical and applied developments

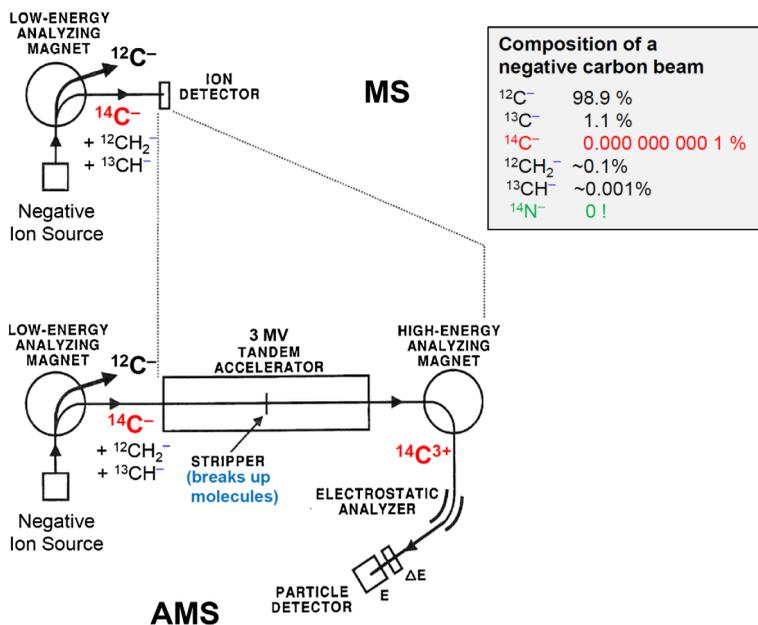


Figure 1. Schematic view of the transition from standard MS to AMS for the detection of ^{14}C . In MS, the background of negative CH molecules overwhelms the ^{14}C signal (see insert box), but is removed in AMS by the stripping process in the tandem accelerator.

of AMS, the present review will primarily discuss its potential for future applications. Since applications of AMS are strongly coupled to technical developments, the current status and future developments in this respect will be discussed first.

2. Technical developments of AMS

Early on, cyclotrons using positive ions [5] as well as tandem accelerators using negative ions [6–8] were used for radiocarbon detection. However, tandem accelerators quickly turned out to be superior. The fact that ^{14}N does not form stable negative ions and therefore does not interfere with ^{14}C (see Figure 1), dominated the development of tandem accelerators for ^{14}C detection. Since most elements form negative ions and can be produced in caesium-beam sputter sources [12,13], the combination of a sputter source with a tandem accelerator became the canonical AMS facility. In rare cases, large accelerators requiring positive ions have been used for AMS experiments of noble gas isotopes [14,15], and of Sm isotopes [16]. It is interesting that an old idea of starting with positive ions, converting them to negative ions without using an accelerator [17], was revived recently [18].

2.1. Accelerator developments

Originally, existing tandem accelerators at nuclear physics laboratories were used for AMS, but soon dedicated AMS facilities were developed [19]. A particularly

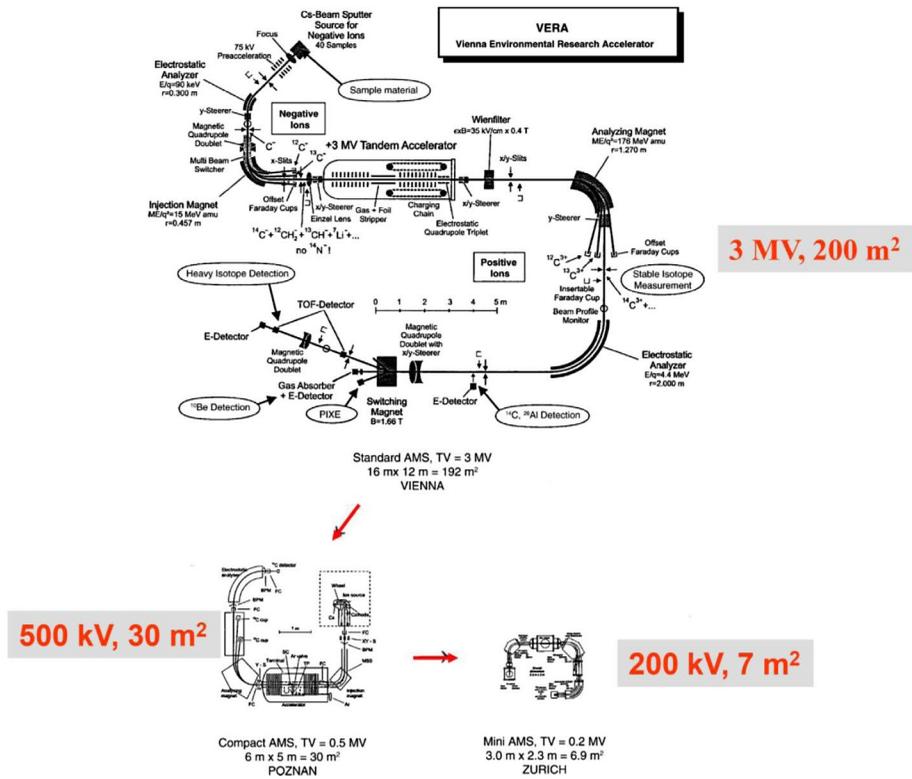


Figure 2. Demonstration of the size reduction of AMS facilities strongly depending on the terminal voltage of the tandem accelerator as pursued by systematic investigations at the ETH Zurich [20–22]. Terminal voltage and floor space requirement are indicated with red labels. The figure is reproduced from Ref. [23].

interesting development happened at the ETH Zurich, where the concept of ‘small is beautiful’ was pursued with ever smaller AMS facilities [20–22]. The dramatic reduction in floor space for AMS facilities by this development is seen in Figure 2.

The development of small AMS facilities such as MICADAS (MIni Carbon Dating System, [22]) was driven by the desire for a ‘table-top’ ¹⁴C AMS system. Although by now more than 50 long-lived radionuclides are being measured with AMS [10], ¹⁴C is by far the most used one (>90%). The applications of ¹⁴C are so vast (see Table 1) that a small machine which can be operated essentially like a standard mass spectrometer is in high demand. The latest development of the 200-kV AMS facility uses permanent magnets for the injection and the high-energy analysis (green MICADAS, [24]). Another step for small ¹⁴C machines – still using negative-ion sputter sources – is the return to MS without an accelerator, which is pursued at the ETH Zurich (M_μCADAS, [25]). Interestingly, as mentioned already above, there is also ¹⁴C positive-ion mass spectrometry (PIMS) developed at SUERC Glasgow [18]. The basic idea of PIMS is to reverse the negative-to-positive ion conversion used in AMS (cf. Figure 1) by starting with positive ions from

Table 1. Overview of research areas where AMS measurements are used (updated from Ref. [10]).

Domain	Research area	Radionuclide ^a
Atmosphere	Production of radionuclides by cosmic rays	^{14}C , ^{10}Be , ^{26}Al , ^{32}Si , ^{36}Cl , ^{39}Ar , ^{81}Kr , ^{129}I
	Chemistry and dynamics of CO , CO_2 , CH_4	^{14}C , ^{14}C
	Mixing of stratospheric and tropospheric air	^{14}C , ^{10}Be
	Releases from nuclear industry	^{14}C , ^{99}Tc , ^{129}I
	Fossil fuel effect, 'dead' CO_2	^{14}C
	Bomb peak from nuclear weapons testing	^{14}C
Biosphere	Radiocarbon dating in archaeology and other fields	^{14}C
	^{14}C calibration (tree rings, corals, sediments, spaleothems)	^{14}C
	Development of radiocalcium dating of bones	^{41}Ca
	Bomb-peak dating (forensic science, age of human cells)	^{14}C
	Microdosing for drug developments	^{14}C
	<i>In vivo</i> tracer studies in plants, animals, humans	^{14}C , ^{26}Al , ^{41}Ca
Hydrosphere	Dating of groundwater (important freshwater resource)	^{14}C , (^{39}Ar), ^{36}Cl , ^{81}Kr , ^{129}I
	Study of global ocean currents	^{14}C , ^{14}C , ^{39}Ar , ^{99}Tc , ^{129}I , ^{231}Pa , ^{236}U
	Paleoclimatic studies in lake and ocean sediments	^{14}C
Cryosphere	Paleoclimatic studies in polar ice sheets and glaciers	^{14}C , ^{10}Be , ^{26}Al , ^{32}Si , ^{36}Cl , (^{81}Kr)
	Tracing solar variability in time (Greenland ice cores)	^{14}C , ^{10}Be , ^{36}Cl
	Bomb-peak record in recent ice	^{36}Cl , ^{41}Ca , ^{129}I
Lithosphere	Exposure dating of rocks (deglaciation, erosion)	^{14}C , ^{10}Be , ^{26}Al , ^{36}Cl , ^{53}Mn
	Paleoclimatic studies in loess	^{14}C , ^{10}Be
	Tectonic plate subduction studies	^{10}Be
	Neutron flux monitor in uranium minerals	^{236}U
Cosmosphere	Cosmogenic nuclides in meteorites and lunar material	^{14}C , ^{10}Be , ^{26}Al , ^{41}Ca , ^{53}Mn , ^{59}Ni , ^{60}Fe
	Live supernova remnants in terrestrial materials	^{26}Al , ^{60}Fe , ^{244}Pu , (^{146}Sm , ^{182}Hf , ^{247}Cm)
	Stable trace isotopes in presolar grains	194 , 195 , 196 , ^{198}Pt
	Geochemical solar neutrino detection	(97 , ^{98}Tc , ^{205}Pb)
	Search for superheavy elements in terrestrial materials	Eka-Th, Ds, Rg, Fl, Eka-Bi, nuclides around $A \sim 300$, $Z \sim 114$
	Search for exotic particles in nature	Free quarks, very heavy isotopes, strange matter
Technosphere	Half-life measurements	^{32}Si , ^{41}Ca , ^{41}Ca , ^{44}Ti , ^{60}Fe , ^{79}Se , ^{126}Sn , ^{146}Sm , ^{182}Hf
	Depth profiling in fusion walls	^3H
	Possible fusion plasma thermometer, $^{27}\text{Al}(n,2n)^{26}\text{Al}$	^{26}Al
	Nuclear reaction studies for nucleosynthesis in stars	^{14}C , ^{10}Be , ^{26}Al , ^{36}Cl , ^{41}Ca , ^{44}Ti , ^{55}Fe , ^{59}Ni , ^{63}Ni , ^{68}Ge , ^{146}Sm , ^{202}Pb , $^{209\text{m}}\text{Bi}$, ^{230}Th , ^{231}Pa
	Neutron dosimetry of the Hiroshima bomb	^{36}Cl , ^{41}Ca , ^{63}Ni
	Nuclear safeguards	146 , 149 , ^{151}Sm , ^{233}U , ^{236}U , ^{237}Np , 239 , 240 , 241 , 242 , ^{244}Pu

^aRadionuclides measured with AMS in the respective research areas. Man-made (anthropogenic) radionuclides are distinguished from natural (cosmogenic) ones by bold isotope symbols. Radionuclides in parenthesis have potential uses in the corresponding research areas, but have not yet reached the required AMS sensitivity.

an electron cyclotron resonance ion source and then producing negative ions in a gas-filled charge exchange cell which suppresses $^{14}\text{N}^-$ and dissociates molecules. It is argued [18] that such a system will be more efficient than standard AMS using sputter sources, especially if ^{14}C measurements of very small gaseous samples (CO_2) is of interest (see Section 2.2 below).

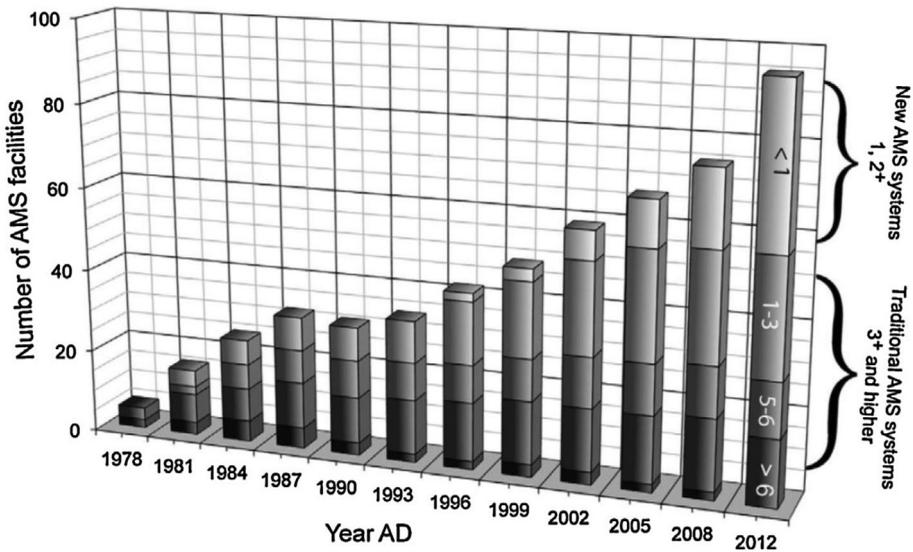


Figure 3. The growth of the number of tandem AMS facilities since 1978, as shown in Figure 4 of Ref. [9]. The different grey shades of the column sections indicate the tandem terminal voltages in MV (numbers are given in the last column in 2012). Also indicated are the charge state which can be reached in the stripping process depending on the terminal voltage. Cyclotrons (bottom sections) were only in use until 2008. The increase in the number of small tandem AMS facilities in the later years is clearly visible. Meanwhile (2016), the number of AMS facilities in the world has grown to well over 100.

The increase in the number of AMS facilities since their invention in 1978 is displayed in Figure 3.

2.2. Reduction of sample size

In the past few years, great progress in the reduction of sample size has been made for ^{14}C measurements both for solid carbon (e.g. [26]), and for gaseous carbon samples (e.g. [27,28]). In order to estimate the limit of sample size, it is convenient to start with a sample of 1 mg C with a modern $^{14}\text{C}/^{12}\text{C}$ isotopic ratio of 1.2×10^{-12} . It contains 6×10^7 ^{14}C atoms. Reducing the sample size to 10 μg C, will still leave one with 6×10^5 ^{14}C atoms. Since the overall efficiency of a ^{14}C AMS system is about 2% (fraction of ^{14}C atoms in the sample actually being counted), one can still collect 1.2×10^4 ^{14}C atoms. The statistical uncertainty is therefore $\sim 1\%$. Going below 10- μg C reduces the statistical uncertainty correspondingly, but the real limitations are uncertainties from various background sources [26]. The direct use of CO_2 gas in the sputter ion source [27,28] avoids the graphitization step for solid C targets [26] and thus reduces the procedural uncertainty. However, the ionization yield for C^- production is considerably lower from CO_2 gas (\sim factor of 10), and finite memory effects are another problem to be addressed. Therefore, overall, solid targets with careful control of systematic uncertainties

[26] still seem to be somewhat superior. On the other hand, the increasing interest in compound-specific ^{14}C measurements with on-line chromatographic analysis prior to the AMS measurement favours the use of gaseous sample material [28].

2.3. Towards general solutions for the isobar problem

By their very nature, radionuclides decay and eventually end up in a stable daughter nuclide. For beta transitions the stable nuclide has the same mass number (A) – and nearly the same mass, but a different atomic number (Z) (e.g. $^{10}\text{Be} \rightarrow ^{10}\text{B}$, $^{14}\text{C} \rightarrow ^{14}\text{N}$, $^{26}\text{Al} \rightarrow ^{26}\text{Mg}$, $^{36}\text{Cl} \rightarrow ^{36}\text{S}$, $^{41}\text{Ca} \rightarrow ^{41}\text{K}$, $^{60}\text{Fe} \rightarrow ^{60}\text{Ni}$, $^{53}\text{Mn} \rightarrow ^{53}\text{Cr}$, $^{90}\text{Zr} \rightarrow ^{90}\text{Mo}$, $^{129}\text{I} \rightarrow ^{129}\text{Xe}$). In any real sample material, the stable isobars are usually orders of magnitude more abundant than the very rare radionuclide one is interested to measure. The ‘easy’ cases for AMS are those where the stable isobars do not form negative ions (^{14}N , ^{26}Mg , ^{129}Xe), and therefore are suppressed already in the ion source. In all other cases, the separation of the radionuclide from its stable isobar interference can be a formidable task. Here, methods developed to identify products in nuclear reaction studies are very useful. Since the energy loss of MeV-ions in matter depends on the atomic number, Z, isobaric pairs such as the ones mentioned above can be distinguished by active energy-loss measurements in gas-ionization or solid-state detectors (e.g. [29]). In addition, time-of-flight measurement can be employed to separate heavy radioisotopes, e.g. ^{129}I , from residual traces of the stable isotope, ^{127}I [29]. Sometimes the stable isobar is so intense that it has to be stopped before the rare isotope reaches the final detector. For example, this can be accomplished by stopping the stable isobar ^{10}B (Z = 5) in a gas cell or foil, while ^{10}Be (Z = 4) reaches a final detector behind the absorber. Another powerful method to separate isobars and block the intense stable component is the gas-filled magnet [30,31]. High energy in the multi-MeV range definitely helps for this latter method. For example, the suppression of ^{60}Ni for the detection of ^{60}Fe is only accomplished at large tandem facilities [32,33]. The detection of actinides offers a certain advantage, because no stable atomic isobars exist in this mass region. However, the removal of break-up products from (stable) molecular isobars injected into the tandem accelerator together with the radionuclide of interest sometimes require considerable effort on the high energy side. Great strides have been made to detect ^{236}U [34] and ^{244}Pu [35] at very low abundances.

2.3.1. Electron photodetachment of negative ions with lasers

The ultimate goal for AMS is to utilize any long-lived radionuclide, which promises an interesting application. This means that one has somehow to solve the isobaric interference problem in a general way. Such a possibility was explored around 1990 at the Weizmann Institute in Rehovot, where the selective photodetachment of negative ions with lasers was investigated [36,37]. This method is useful when the electron affinity (EA) of the unwanted negative ion is smaller than the one of the wanted one. Hence the suppression of $^{36}\text{S}^-$ ions (EA = 2.077 eV) for the detection

of ^{36}Cl (EA = 3.613 eV) [36] and the suppression of $^{59}\text{Co}^-$ ions (EA = 0.662 eV) for the detection of ^{59}Ni (EA = 1.156 eV) [37] could be demonstrated. However, for the relatively swift ions (150 keV) from the negative ion injector of the 14-MV Pelletron tandem accelerator, an effective laser-ion interaction was only possible with a pulsed laser system (Nd:YAG, repetition rate 30 Hz, pulse length 100 ns). This resulted in a very low duty factor, of no practical use for AMS experiments with rare radionuclides. Some 20 years later, efficient methods to slow down negative ions extracted from an ion source to very low energies (~ 100 eV) in a biased He-filled radiofrequency quadrupole ‘ion cooler’ were developed at Oak Ridge National Lab [38], and refined at the Universities of Gothenburg and Vienna [39,40]. This, then, allows interaction with a CW laser system solving the duty factor problem mentioned above. After an extensive test phase in Vienna [41], an interaction system of lasers with negative ions is currently being installed at the injector of the VERA AMS system.

2.3.2. Selective chemistry in reaction cells

An alternative way to suppress unwanted negative ions is a selective chemistry in a reaction cell, which is being pursued at IsoTrace in Toronto [42], and more recently at the André E. Lalonde AMS Laboratory in Ottawa [43]. Together with the laser method, this method will also help to make essentially all long-lived radionuclides available for AMS measurements. If this goal can be reached in the near future, it will allow one to pursue new applications, some of which will be mentioned in the following discussion on trends of AMS applications.

3. Applications of AMS – now and in the future

A rather comprehensive review of applications of AMS was published in 2013 [10], and the reader is referred to it for the enormous breadth of applications covering essentially every domain of our environment at large. Traces of both cosmogenic and anthropogenic radionuclides can be measured with AMS in the atmosphere, biosphere, hydrosphere, cryosphere, lithosphere, cosmosphere, and technosphere (see Table 1). The table lists research areas in these seven domains of the environment at large, and the corresponding long-lived radionuclides which are measured with AMS. The ubiquitous presence of ^{14}C in almost all research areas emphasizes the importance of this unique radionuclide. Half-lives for the listed radionuclides ranging from approximately 10 to 10^8 years, can be found in [10].

In the following an attempt will be made to point out areas where AMS measurements can make a difference, provided that the advance of technical improvements pointed out above will allow one to use the full spectrum of trace isotopes across the nuclear chart, and some other problems limiting currently certain applications can be solved. Therefore it is more a wish list than hard predictions what can be done in the future with AMS.

3.1. Archaeology

Willard Libby received the 1960 Nobel Prize in Chemistry ‘for his method to use carbon-14 for age determination in archaeology, geophysics, and other branches of physics’. This still forms the basis for ^{14}C dating, but considerable improvements came along with AMS, and other radioisotopes are being used as well in the fields pointed out above.

3.1.1. ^{14}C dating

It is clear that ^{14}C dating will continue to dominate the field of archaeology, and both the increase of small AMS facilities and the reduction of sample material into the few- μg range will open up the field to more applications. In particular, small samples will allow quasi non-destructive sampling of precious objects. Although radiocarbon dating has made a big difference in establishing absolute time frames in archaeology, the ‘wiggly’ calibration curve often limits the precision [44]. There have been some attempts to overcome this problem by developing absolute ^{14}C dating [45], i.e. to measure both ^{14}C and its decay product $^{14}\text{N}^*$, and not only the $^{14}\text{C}/^{12}\text{C}$ ratio as in standard ^{14}C dating. It can easily be shown that in absolute dating the age can be calculated from the relation $t = (t_{1/2} / \ln 2) \times \ln(1 + ^{14}\text{N}^*/^{14}\text{C})$. However, as to our knowledge, nobody has yet succeeded to measure the few ‘drops’ of radiogenic $^{14}\text{N}^*$ in the ‘ocean’ of environmental ^{14}N . Since for the foreseeable future, ^{14}C dating will depend on a calibration curve, the validity of the global calibration curve [46] on every place on Earth is important. Small regional shifts have been observed [47–49], but usually they are insignificant as compared to the inherent uncertainty of the age determination. An important task for the future is to demonstrate – and to hopefully convince even the staunchest skeptics of the ^{14}C dating method – that the steady improvement of the method (field work, archaeological context, sample identification and preparation, calibration) leads to much more reliable age determinations as compared to the early days [50].

3.1.2. ^{41}Ca dating – still a dream to come true

The half-life of ^{41}Ca is very close to 100,000 years, i.e. $(9.94 \pm 0.15) \times 10^4$ year, [51]), which is considerable longer than the half-life of ^{14}C (5700 year). Therefore, a ^{41}Ca dating method could cover the last few hundred thousand years, which includes the whole period of Neanderthal and anatomically modern man. Since fossil bones are the most direct witnesses and Ca is a major constituent of bone, $^{41}\text{Ca}/^{40}\text{Ca}$ ratio measurements with AMS have been explored for possible radiocalcium dating [52–54]. However, several problems will have to be overcome before a viable ^{41}Ca dating method can be established: (i) The major production mechanism of ^{41}Ca is the $^{40}\text{Ca}(n, \gamma)^{41}\text{Ca}$ reaction of cosmic-ray secondary neutrons on the surface of the Earth, mainly in carbonate rocks [55]. (ii) In contrast to ^{14}C , which is well-mixed in the atmosphere as $^{14}\text{CO}_2$, ^{41}Ca does not form a gas and therefore a global calibration is not possible. (iii) ^{41}Ca decays by electron-capture

to $^{41}\text{K}^*$, and absolute dating through the measurement of $^{41}\text{Ca}/^{41}\text{K}^*$ ratios may be possible. High-precision isotopic ratio measurements of potassium, with uncertainties in the ppm range, may allow one to trace the minute additions of $^{41}\text{K}^*$ to ubiquitous ^{41}K . (iv) Calcium phosphate ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$) is the main constituent of the bio-mineral apatite in bones, and the small recoil energy of $^{41}\text{K}^*$ (~ 2.2 eV) due to the neutrino emitted in the EC decay of ^{41}Ca , may lead to a good confinement of $^{41}\text{K}^*$ within the apatite crystals. (v) In order to prevent a post-mortem build-up of ^{41}Ca , a fossil bone has to be located underground (e.g. in a cave) in order to be shielded from cosmogenic neutrons.

3.1.3. Exposure dating with ^{10}Be , ^{26}Al , and ^{36}Cl

Exposure dating utilizes the *in situ* production of long-lived radionuclides by cosmic-ray secondaries (neutrons, muons) in surface rocks. This method is widely used in geomorphology and geophysics (e.g. [56,57], see also Section 3.5.2.). In the context of archaeology, the burial of previously surface-exposed quartz grains with a known production ratio for two radionuclides of different half-lives such as ^{10}Be (1.4×10^6 year) and ^{26}Al (7.2×10^5 year) has been used as a chronometer through the change of the atom ratio $^{26}\text{Al}/^{10}\text{Be}$ with time. By this method the age of the famous Peking man was found to be 0.77 ± 0.08 million years [58], significantly larger than previously assumed (~ 0.5 million years). Another interesting example of surface exposure dating in connection with archaeology was the use of *in situ* produced cosmogenic ^{36}Cl (3.0×10^5 year) from a limestone rock slide which apparently sealed the Chauvet-Pont d'Arc cave around 21,000 years ago [59], thus preserving the famous Upper Palaeolithic cave art [60].

3.2. Astrophysics

It is a well-accepted view that most elements beyond hydrogen and helium are synthesized in stars [61,62]. The great progress in observational astronomy and astrophysical theories, combined with both nuclear astrophysics experiments in the lab and nuclear theories, generated a multitude of stellar scenarios, which need to be tested 'somehow'. Here a few cases of such tests will be briefly described, where AMS measurements made a difference.

3.2.1. The detection of 'close-by' supernovae with ^{60}Fe

Supernovae are explosive stellar events which typically produce neutron-rich isotopes of many elements by the r-process (rapid neutron capture). A rather unique case is ^{60}Fe with a half-life of 2.6 million years [33]. Because of a major interference with the stable isobar ^{60}Ni , a detection of ^{60}Fe was so far only possible at large AMS facility such as the 14-MV tandem accelerators in Munich and in Canberra. First traces of live ^{60}Fe were found in a deep-sea ferromanganese crust, and interpreted as stellar debris of a supernova explosion some 2 million years ago [63,64]. Intensive investigations for traces of ^{60}Fe in other deep-sea material

have culminated recently in the notion that more than one supernova took off within about 300 light-years distance from Earth around 2.2 million years ago [65,66]. In addition, interstellar ^{60}Fe has now also been observed on the surface of the Moon [67].

Whether ^{60}Fe can also be measured at smaller AMS facility in the future will depend on the success of the new isobar suppressions techniques discussed in Section 2.3.1.

3.2.2. Neutron star mergers as likely candidates for ^{244}Pu production

The neutron-rich radionuclide ^{244}Pu has a half-life of 80 million years [68]. It is the longest-lived nuclide beyond ^{238}U and is exclusively produced by the r-process in neutron-rich stellar environments. Since there are no stable nuclides in the actinide region, ^{244}Pu can be measured also at smaller AMS facilities such as VERA in Vienna. The measurement of a depth profile in a very old (~65 million years) deep-sea ferromanganese crust revealed significantly less ^{244}Pu than expected from supernova explosions [35]. In fact, it has been suggested by astrophysical modelling that neutron star mergers are the likely source of ^{244}Pu [69].

3.2.3. Has ^{244}Pu survived from the early solar system?

The existence of ^{244}Pu at the formation of the solar systems was hinted from Xe isotope anomalies produced by spontaneous fission of ^{244}Pu [70], leaving fingerprints in meteorites. This hypothesis was later confirmed by measuring the spontaneous fission spectrum of ^{244}Pu in the laboratory [71]. In 1971, the direct detection of ^{244}Pu in a rare earth mineral (bastnäsite) on Earth was reported [72]. This was a surprising result because it meant that today – after a decay of 56 half-lives – measurable traces of ^{244}Pu were left in the rare earth mineral. The Munich AMS group performed a new search for ^{244}Pu , also in bastnäsite [73]. No ^{244}Pu events were observed, resulting in a ^{244}Pu concentration limit 10 times lower than the one observed in the Los Alamos experiment [72].

3.2.4. A new half-life for ^{146}Sm

Ever since the pioneering work on the $^{26}\text{Al} \rightarrow ^{26}\text{Mg}$ system [74,75], anomalies in the abundance of stable nuclides in meteorites caused by *in situ* decay of ‘short-lived’ (million-year) radionuclides have been used as fast-running clocks for the formation of the Early Solar System [76]. The alpha decay of proton-rich ^{146}Sm to ^{142}Nd forms one of such systems. Recently, the half-life of ^{146}Sm has been re-measured with AMS at the ATLAS linear accelerator at Argonne [16]. It was found to be 66 ± 7 million years, substantially shorter than the previously used value of 103 ± 5 million years. The thus re-calibrated ^{146}Sm - ^{142}Nd clock has implications for the chronology of the solar system formation and planetary differentiation [77]. It may also shed light on p-process nucleosynthesis of ^{146}Sm [78].

3.2.5. ^{182}Hf as a versatile astrophysical chronometer

The neutron-rich radionuclide ^{182}Hf (half-life = 8.9 ± 0.1 million years) decays via ^{182}Ta (114 d) to stable ^{182}W . High-precision MS of stable W isotopes used the ^{182}Hf - ^{182}W clock in iron meteorites to extract information on core formation and accretion of protoplanets in the solar system formation [79]. Since ^{182}Hf can be formed both via s- and r-process [80], it could be used in a similar way as ^{60}Fe above, provided that live ^{182}Hf could be detected with AMS in suitable terrestrial archives. Since Hf does not form negative ions, HfF_n^- molecules were explored at VERA, and $^{182}\text{HfF}_5^-$ was found to suppress the isobaric interference from $^{182}\text{WF}_5^-$ best. In this way, a $^{182}\text{Hf}/^{180}\text{Hf}$ detection limit of $\sim 10^{-11}$ was reached [81]. It is hoped that the laser detachment method described in Section 2.3.1 will allow one to push the sensitivity of ^{182}Hf detection into the realm where a stellar signal in a terrestrial archive can be detected.

3.2.6. Search for superheavy elements in nature

Almost 50 years ago an ‘island of stability’ was predicted around mass number 300 from shell model calculations (e.g. [82]). Since $Z = 114$ and $N = 184$ were the new ‘magic’ numbers, the corresponding centre of the island could not be reached with heavy ion reactions of any conceivable target-projectile combination. However, great effort was put into producing superheavy elements (SHEs) with lower neutron numbers via heavy-ion reactions at Berkeley, Dubna, GSI, and Riken. In this way SHEs with Z from 104 to 118 were formed arriving at the south-west ‘shore’ of the island of stability [83]. An alternative way to find SHEs are searches for traces of SHEs in Nature assuming that they were produced in supernovae, are long-lived enough (≥ 100 million years), and follow their chemical homologue [84] through the geochemical history of the Earth. An early AMS search was performed for Eka-Platinum $^{294}110$ (now ^{294}Ds) at the University of Pennsylvania, setting an abundance limit of 10^{-11} for this SHE nuclide in a Placer platinum nugget [85]. More recently, very surprising results were reported by the group of Marinov et al. from the Hebrew University Jerusalem, who performed experiments with high-resolution inductively coupled plasma – sector field mass spectrometry (ICP-SF-MS), and found evidence for several long-lived neutron deficient SHEs [86,87], and in particular also for the possible existence of $^{292}\text{Eka-Th}$ in natural Thorium [88]. However, AMS experiments in Munich [89,90] and in Vienna [91–93] could not confirm these results with orders of magnitude higher abundance limits as compared to the MS experiments (Figure 4). These findings, which clearly demonstrate the power of AMS over MS by identifying the observed events unambiguously, are further elaborated by a review [94] in the Special Issue on Superheavy Elements in Nuclear Physics A [95].

3.2.7. Measuring the solar neutrino flux in the past

It is well-known that neutrinos are the only messengers from the interior of the sun reaching the Earth, and the present-day solar neutrino flux has been measured

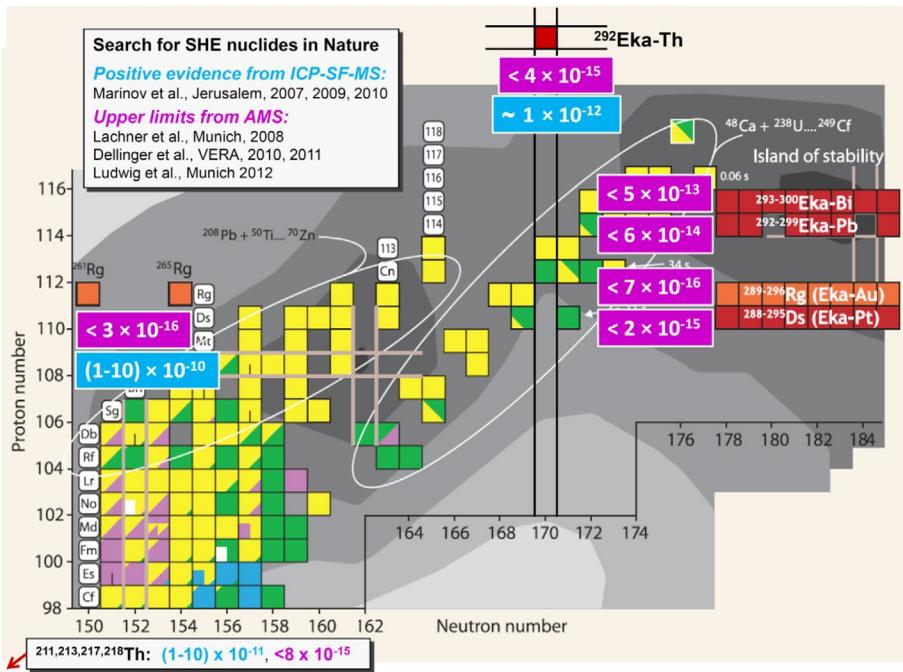


Figure 4. Summary of the results for searches of superheavy nuclides in terrestrial materials [96]. The basic layout of the figure is from [97], depicting the upper end of the chart of nuclides. The shades of grey in the background indicate the relative stability of nuclides due to shell model corrections (darker means more stable). Nuclides marked in orange and red have been measured with AMS. Abundance limits measured with respect to the corresponding host material (e.g. Rg isotopes (Eka-Au) were searched for in gold nuggets) are given in violet boxes. The positive evidence of the Marinov experiments is shown in the blue boxes. References for the various experiments indicated in the insert are referred to in Section 3.2.5.

with different large-volume detectors in underground laboratories. Once the neutrino oscillation problem was solved, the measured flux was largely consistent with the solar model predictions [98]. In order to know something about the solar neutrino flux in the past, one could use long-lived radioisotopes which are produced by solar neutrino interaction on suitable target isotopes in well-shielded underground mineral deposits to avoid cosmic-ray induced background production. Several Systems were proposed:

$^{205}\text{Tl}(\nu_e, e^-)^{205}\text{Pb}(t_{1/2} = 1.7 \times 10^7 \text{ year})$ [99], $^{81}\text{Br}(\nu_e, e^-)^{81}\text{Kr}(2.3 \times 10^5 \text{ year})$ [100], $^{97}\text{Mo}(\nu_e, e^-)^{97}\text{Tc}(2.6 \times 10^6 \text{ year})$ and $^{98}\text{Mo}(\nu_e, e^-)^{98}\text{Tc}(4.2 \times 10^6 \text{ year})$ [101], and $^{126}\text{Te}(\nu_e, e^-)^{126}\text{I}(13 \text{ d}, \beta^-)^{126}\text{Xe}$ [102]. In all cases, a very careful evaluation of background reactions producing the same isotope as the neutrinos (e.g. cosmic-ray induced reactions) is mandatory. In addition, the transition probability for the neutrino-induced inverse β -decay reactions needs to be known. So far none of these proposals developed into a real project, and currently only the ^{205}Tl - ^{205}Pb system is actively being pursued. In this case a crucial quantity is the overburden of the rather shallow deposit of the mineral lorandite (TlAsS_2) in the Allchar mine

in Macedonia, which was recently explored with an erosion rate study using *in situ* produced cosmogenic ^{26}Al , ^{36}Cl , ^3He , and ^{21}Ne [103]. Eventually, AMS may also be used to measure ^{205}Pb with a large accelerator [104]. It is clear that all of the proposed systems for the measurement of the past solar neutrino flux are very challenging, but the unique potential to trace the status of our sun in the past will hopefully be enough incentive for somebody to launch an all-out attempt on this interesting problem.

3.3. Testing the Pauli exclusion principle

The Pauli exclusion principle [PEP; 105] states that two identical fermions (e.g. electrons or nucleons) cannot occupy the same quantum state simultaneously. The PEP would be violated if, for example [106], three atomic electrons would occupy the atomic K shell or if three protons or three neutrons would be in the nuclear $1s_{1/2}$ shell. This concept allowed the Munich AMS group to search for a violation of PEP by looking for non-Paulian atoms of ^{20}Ne in Fluorine and for non-Paulian nuclei of ^5Li in Lithium [106]. Very low limits for a violation of PEP of $<10^{-21}$ and $<10^{-14}$ were found for non-Paulian ^{20}Ne in normal ^{20}Ne and for non-Paulian ^5Li in Lithium, respectively. A test of non-Paulian beryllium with all four electrons in the K shell (helium-like atoms) was performed with AMS by the PRIME Lab of Purdue University [107]. No non-Paulian Be events were observed and stringent concentration limits were set for a variety of materials investigated.

3.4. The usefulness of the ^{14}C bomb peak

In 1963, the USA, the Sovietunion, and the UK signed the limited nuclear test ban treaty, which stopped above-ground testing of nuclear weapons. It was realized at the highest political level that the relentless race for ever more destructive nuclear power, which started in the 1950s, polluted our world globally with radioactive fallout to such an extent that in the middle of the cold war a ‘reasonable’ decision was made. Besides the fallout of radioactivity from fission products and bomb material (e.g. ^{239}Pu), the intense neutron-flux from hydrogen bomb testing produced ^{14}C from ^{14}N , just like the secondary neutrons from cosmic-ray interaction with the atmosphere (Figure 5). An increase of ^{14}C in atmospheric CO_2 was noticed early on [108]. From then on ^{14}C was monitored in atmospheric CO_2 of the northern and southern hemisphere [109]. The rapid increase in the early 1960s and the decline after the 1963 test ban treaty (due to the exchange of CO_2 with the other carbon reservoirs on Earth) created the atmospheric ^{14}C bomb peak (Figure 6). This, then, led to a variety of interesting applications [110].

One of the most astounding applications of the ^{14}C bomb peak is the dating of the birth of cells in humans, developed at the Department of Cell and Molecular Biology of the Karolinska Institute in Stockholm [111]. In Figure 6(A) the principle of the method is depicted, and in Figure 6(B) significant neurogenesis in

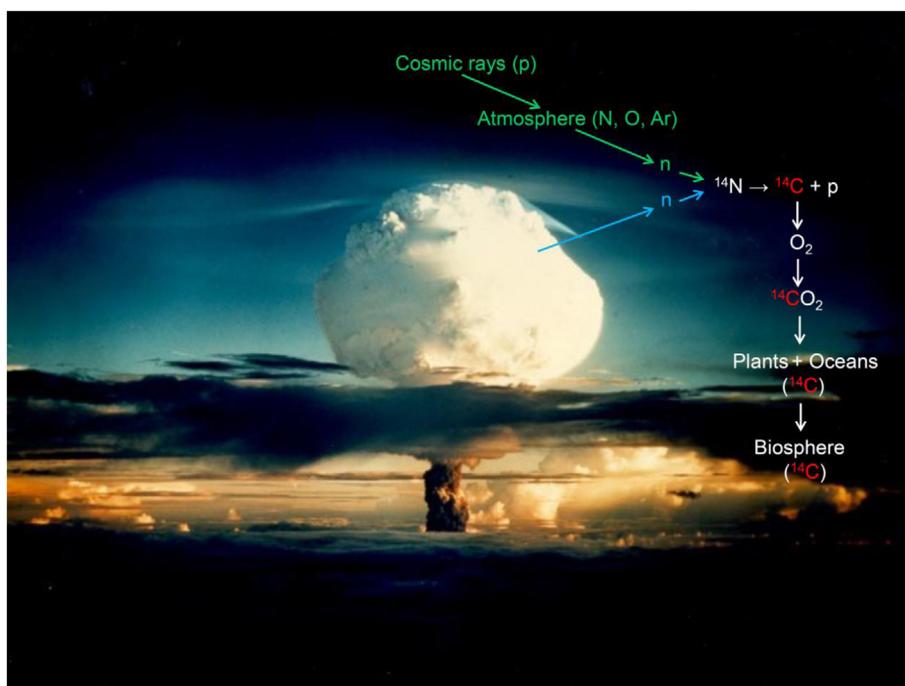


Figure 5. Picture of the first hydrogen bomb test of the USA on Eniwetok Atoll of the Marshall Islands in the Pacific Ocean on 1 November 1952. The explosive power was 10.4 Megatons TNT, about seven hundred times the one of the Hiroshima bomb. The simplified schematics indicates that neutrons from the bomb tests convert ^{14}N into ^{14}C , just like the neutrons emerging from the spallation of atmospheric nuclei with high-energy protons from cosmic rays. This led to a doubling of the $^{14}\text{C}/^{12}\text{C}$ ratio in atmospheric CO_2 in a few years and created the ' ^{14}C bomb peak' [109].

the hippocampus of adult human brains was found [112]. It thus considerably widened our view of brain plasticity, i.e. changes of the human brain after early childhood.

It is also possible to use the ^{14}C bomb peak to uncover forgeries in the arts (e.g. [113]), and to discover illicit trade of ivory according to the Convention on International Trade in Endangered Species of Wild Fauna and Flora (Washington 1973). In addition, since atmospheric CO_2 was labelled with bomb ^{14}C at a precisely known time, this signal allows one to study in great detail the dynamics of the carbon cycle in the atmosphere (e.g. [114]), in the hydrosphere (groundwater, ocean), and in soil. It may help for a better understanding of the sequestration of CO_2 in the ocean and on land, an important issue in the debate about the human impact on the climate through CO_2 emissions from burning fossil fuel.

3.5. Earth sciences

The Earth is, of course, the place where we live, and a better understanding of every aspect of it is at the basis of our sustained presence on this planet. AMS

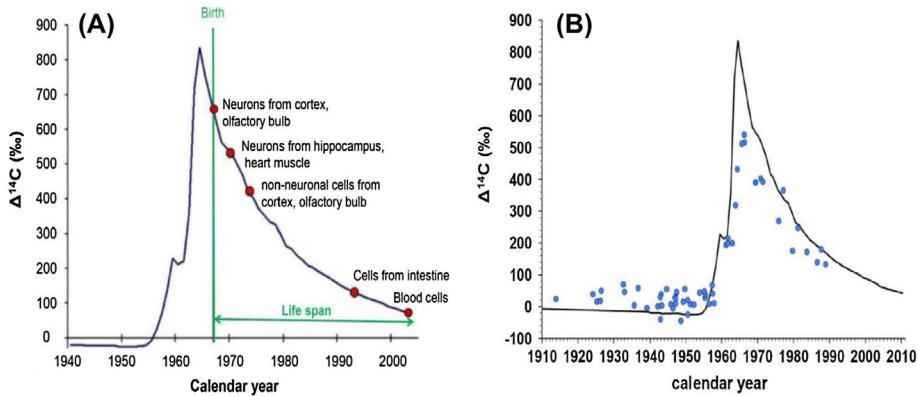


Figure 6. Use of the ^{14}C bomb peak for dating human cells. The solid curve follows the deviation of ^{14}C from the natural reference value ($\Delta^{14}\text{C} = 0$). The red dots in Figure 6(A) indicate the birth date of different cells after birth of an individual who lived from 1968 to 2004. The dates were determined from measuring ^{14}C in DNA extracted from the respective cells [111]. Figure 6(B) shows the results for ^{14}C measurements in the DNA for neurons in the hippocampus of 57 individuals [112]. The blue dots give the respective $\Delta^{14}\text{C}$ values which are plotted at the birth date of the individual. For people born before the bomb peak, a value above zero clearly indicate neurogenesis after birth.

contributes to this by tracing cosmogenic and anthropogenic radioisotopes into many domains (see Table 1). A more general discussion of AMS measurements in the different areas of Earth sciences (atmosphere, hydrosphere, cryosphere, lithosphere) can be found in Ref. [10]. Here we only discuss particular aspects of the ice coverage on Earth, where AMS can make a difference.

3.5.1. Oldest ice cores

It is well known that part of the Earth was periodically covered with large ice sheets during the Pleistocene (last 2.5 million years). In the first half of the twentieth century, Milutin Milankovic described the glacial/cold – interglacial/warm periodicity with his theory of changes of solar insolation through the variation of Earth's orbital parameters [115]. This was later confirmed by the analysis of sediment cores [116] and ice cores from Antarctica [117]. The latter goes back about 800,000 years. Ice cores both from Greenland and Antarctica contain a wealth of information on the paleoclimate, and there is great interest to extend the time range from currently 800,000 years [117] to about 1.5 million years. There are efforts under way to find the best location in Antarctica for such old ice [118]. Absolute dating methods for old ice would be an important asset, and chronometers based on ratios of cosmogenic radioisotopes with different half-lives such as $^{10}\text{Be}/^{26}\text{Al}$ [119] and $^{10}\text{Be}/^{36}\text{Cl}$ [120] are being explored. However, it is possible that the noble gas radioisotope ^{81}Kr (2.3×10^5 year) due to its chemical inertness is superior for dating old ice. In this case, not AMS but ATTA (Atom Trap Trace Analysis) will probably be used, which has already been applied for the dating of old surface ice from the Taylor Glacier in Antarctica [121].

3.5.2. Glacial changes

The last glacial period (commonly called the Ice Age) ended around 11,500 years ago, and was followed by the interglacial Holocene, which lasts until today. However, Paul Crutzen raised the question, whether man's impact on the Earth's system during the past 300 years constitutes a new geological period, which one might call Anthropocene [122]. The Anthropocene has recently been discussed already as a geologically distinct period [123].

Although ice core records from the last 10,000 years show relatively stable temperature conditions, Alpine glaciers both in the northern hemisphere (European Alps) and the southern hemisphere (New Zealand Alps) advanced and retreated several times during this period. The chronology of these movements can be traced with *in situ* produced cosmogenic radioisotopes (^{10}Be , ^{14}C , ^{26}Al , ^{36}Cl) by exposure dating of moraines (e.g. [124,125]), by ^{14}C dating of organic material (wood and peat) imbedded in moraines and/or released from receding glaciers (e.g. [126–128]). Temperature variations in the European Alps have been traced by tree line movement since it moves by about 100 m for an average summer temperature change of 0.6–0.7 °C (e.g. [129]). As a result of these investigations, a picture of Holocene glacier and temperature fluctuations for the European Alps emerges, which is summarized in Figure 7. The general trend of temperature curve indicates that the first half of the Holocene was on the average warmer than the second half. Temperatures started to decline just about at the time of the Iceman 5000 years ago.

Glacial changes and tree line movements can be considered to be proxies for climatic changes, but it is still discussed to what extent those changes are regional or global. For example there is some indication that glacial movements at the southern hemisphere are out of phase with those from the northern hemisphere [124]. In addition, the role of activity changes of the sun is discussed as a possible trigger for these climate changes [130,131].

3.6. Anthropogenic radioisotopes

The summary of research fields where AMS is being used (Table 1) shows that anthropogenic radioisotopes are ubiquitous. Some constitute a serious background in cases where one is interested to utilize the natural abundance only. An example is ^{129}I , which is released from nuclear fuel reprocessing plants, and $^{129}\text{I}/^{127}\text{I}$ ratios in the general environment can be orders of magnitude higher as compared to the natural signal of ^{129}I [133]. However, since the locations and timing of anthropogenic ^{129}I releases are well known, it can also be used as a tracer to study ocean currents [134]. Due to the way anthropogenic radioisotopes are being used and/or brought into the environment, they can be divided into two categories: Intentional and unintentional. In the following a few examples for both categories will be given.

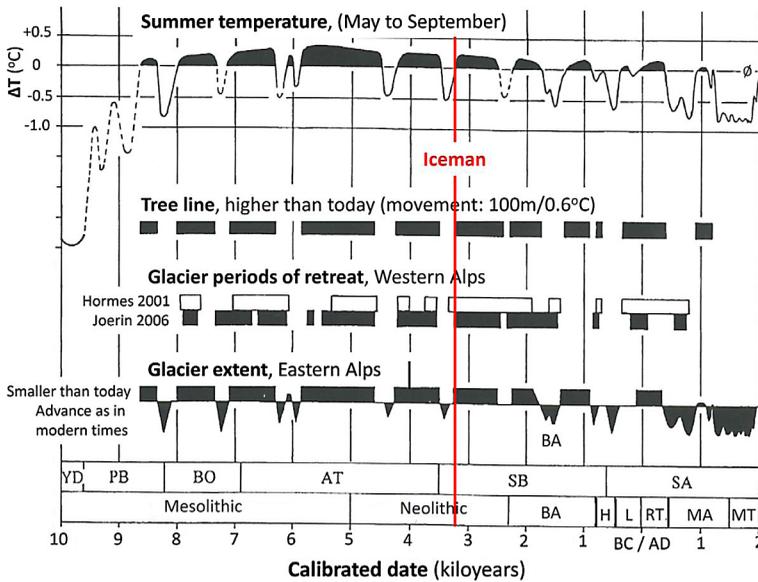


Figure 7. This figure is reproduced from Ref. [132], and shows variations of glaciers, tree lines and average summer temperature variations for the European Alps throughout the Holocene. The periods of smaller glaciers and higher tree lines are indicated with box symbols. Glacial advances are indicated with filled triangles and filled curves. The largest advance took place during the Little Ice Age (~1300–1850 AD). The top curve (hand-drawn with some freedom of the shape) depicts the relative summer temperature variations deduced from the tree line movement. The mean temperature between 1900 and 2000 AD is used as zero-degree reference. The red line marks the time of the Iceman who lived some 5000 years ago [132]. At the bottom of the figure the paleoclimatic periods (YD = Younger Dryas; PB = Preboreal; BO = Boreal; AT = Atlantic; SB = Subboreal; SA = Subatlantic) and the archaeological periods (BA = Bronze Age; H = Hallstatt period; L = La Tène period; L + H = Iron Age; RT = Roman times; MA = Middle Ages; MT = Modern times) are indicated.

3.6.1. Biomedical research with radioisotopes

The use of man-made radioisotopes in the field of medicine for research, diagnostics and therapy is well known. AMS plays an important role in biomedical research through its outstanding detection sensitivity of long-lived radioisotopes [135]. The very small amount of radioisotopes required for testing new drugs allowed one to study the metabolism and pharmacokinetics of these drugs by microdosing of humans, considerably reducing the time for a new drug development [136]. Most important is the labelling of drugs with ^{14}C , and the development of small radiocarbon AMS facilities [137] has encouraged pharmaceutical companies to engage in this field, e.g. [138]. Other radioisotopes such as ^{26}Al and ^{41}Ca can be administered to humans in large (atom) amounts. Because of their long half-lives they do not produce much radioactivity. So far, there have only been a few exploratory experiments with ^{26}Al and ^{41}Ca , see [10]. The use of ^{41}Ca looked promising in connection with bone metabolism [139], However, a real drug development, e.g. in connection with osteoporosis, has yet to come.

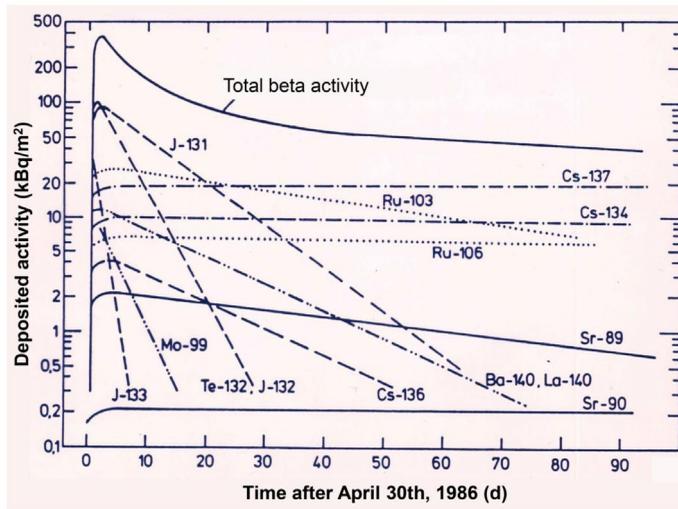


Figure 8. Fallout from the Chernobyl reactor accident measured at the GSF Neuherberg near Munich [146].

3.6.2. Unintentionally produced radioisotopes

Probably the most interesting example of using unintentionally produced radioisotopes is the ^{14}C bomb peak described already in Section 3.3. Bomb ^{14}C has also been used to study the uptake of CO_2 in the ocean [140], an important contribution to a better understanding of the fate of atmospheric CO_2 additions due to fossil fuel emissions. Another application of the ^{14}C bomb pulse is the study of recent speleothems, particularly when they grow in cave systems which form part of the groundwater supply to large cities, e.g. for Sydney [141]. From such studies one can learn something about the recharge time of important groundwater systems. Nuclear weapons testing produced also a number of other radionuclides (e.g. ^{36}Cl , ^{41}Ca , ^{90}Sr , ^{137}Cs). For example, the ^{41}Ca bomb pulse has been measured in glacier ice of the European Alps, and atmospheric transport of radionuclides has been described by suitable transport models [142]. Recently, ^{236}U (2.3×10^7 year) has been explored as an oceanographic tracer [143].

3.6.3. Nuclear reactor accidents

The most serious unintentional releases of radionuclides happened at nuclear reactor accidents. Well-known are the accidents of Three Mile Island (1979), Chernobyl (1986) and Fukushima (2011). The considerable fallout of the fission products ^{131}I (half-life = 8.0 days) and ^{129}I (16 million years) from the Chernobyl accidents in the Munich area, allowed the measurement of the $^{129}\text{I}/^{131}\text{I}$ isotope ratio, which was used to determine the running time of the reactor (~ 2 years) before the explosion [144]. While short-lived ^{131}I was measured from the 364-keV γ -line with Ge detectors, long-lived ^{129}I was measured with AMS at the 14-MV Pelletron tandem accelerator of the Weizmann Institute. Figure 8 shows

the radioactivity for several radioisotopes deposited in the Munich area after the Chernobyl accident. A comparison with the Fukushima fallout [145] indicates that Chernobyl released roughly 10 times more radioactivity than Fukushima.

Radioactive contamination of areas immediately adjacent to the damaged reactors is, of course, a serious problem. Efficient methods for decontamination and remediation of these areas are urgently needed. This seems to be a lesson one has to learn from such accidents. On the other hand, the release of long-lived fission products into the environment allows one to trace migrations of unintentionally labelled animals (e.g. fish) across entire oceans, mostly using AMS as the analytical method of choice.

4. Conclusion

This review of AMS discusses a few selected topics, which are necessarily biased by the interest and/or involvement of the author. As mentioned already in the introduction, many reviews of AMS already exist, and the two latest ones [9,10] are recommended for a more complete overview of the field. In general, AMS can truly be called ‘The art of identifying and counting rare atoms one by one’. As such it can literally be used for investigations in every domain of our environment at large. The combination of refined AMS techniques described in the technical part of this review, together with some challenging applications touched upon also here, promises a bright future for AMS.

Acknowledgements

The author has been lucky to be involved with AMS since its beginning in the late 1970s. The reason that over the years he didn't lose interest in the field is on the one hand based on the enormous breadth of applications the AMS method provides, and on the other hand on countless discussions with colleagues from AMS and many different fields all over the world. He gratefully acknowledges the benefit of these discussions, and of useful comments by an anonymous reviewer.

Disclosure statement

No potential conflict of interest was reported by the author.

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